(141d) Role of CeO2 In the Total Oxidation of Toluene Over CuO-CeO2/Al2O3

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Introduction

Benzene, toluene and xylene(BTX), are considered to be three major carcinogens and their emission in theenvironment has to be controlled. Among the destructive technologies, catalyticoxidation is the most promising approach for the abatement of Volatile OrganicCompounds (VOCs) owing to its advantages including high efficiency, lowoperating temperature and no secondary pollution[1].The performance of the catalyst determines the effectiveness of this technique.

Supported or unsupported noblemetal catalysts are used for complete oxidation of VOCs, but high costs limittheir wide application, thus giving way to transition metal oxides such ascopper oxide. These are less active at lower temperatures but present comparableactivity at higher temperatures and have high catalyst loading capabilities[2-6].

However, a pure copper-basedcatalyst is less active and stable in the presence of water vapor and/or CO_2in the gas mixture. At the same time, copper catalysts promoted by ceria showbetter catalytic performance for the complete oxidation of toluene, propane, benzeneand p-xylene than unpromoted copper catalysts[7,8]as well as improved activity in the presence of oxidation products $CO_2$and water [9]. Ceria as a promoter forsupported CuO has shown several advantages: (a) ceria stabilizes the dispersionof the active component[10,11]; (b) metal/ceriainteractions strongly affect their redox and catalytic properties; (c) ceriaalso acts as an oxygen storing component due to the presence of mixed oxidationstates (3+/4+) of cerium; (d) copper-doped CeO_2 can improve theoxygen storage capacity, diffusivity and redox properties, which are attributedto the formation of structural defects.

However, it is still unclear howcopper and ceria interact with each other and promote catalytic activity. Thequestions addressed in this study are: (1) Assistance of CeO_2 in theoxidation of reduced copper species, (2) the crucial copper species inducingthe coppeR&Deg;Ceria interaction, (3) the active sites of coppeR&Deg;Ceria system fortoluene oxidation, (4) the role of ceria in decreasing the negative effect of thepresence of water and CO_2, (5) the enhancement of catalytic activitydue to coppeR&Deg;Ceria interaction

In this study the binary mixedoxide, CuO-CeO_2/g-Al_2O_3, hasbeen investigated in detail in comparison to its corresponding single-oxidecomponents CuO/g-Al_2O_3, CeO_2/g-Al_2O_3in order to correlate catalytic activity towards total oxidation oftoluene with their physicochemical characterization. A transient responsetechnique with millisecond time scale[12] was used to investigate thecatalytic activity and influence of H_2O and CO_2 on thecatalytic behavior. The structure of the catalysts was investigated by the useof high resolution electron microscopy (HRTEM), selected area electrondiffraction (SAED), X-ray diffraction (XRD) and X-ray absorption Spectroscopy(XAS).

Experimental procedure

The $CuO-CeO_2/\gamma-Al_2O_3$,$CuO/\gamma-Al_2O_3$ and $CeO_2/\gamma-Al_2O_3$catalysts were synthesized via impregnation of $\gamma-Al_2O_3$with $Cu(NO_3)_2 2.5H_2O$ and/or $Ce(NO_3)_4 9H_2O$ precursors, followed by drying at 357K for 8h andcalcination above 973 K for 8h in air. 10mg of 250-500mm particles were used for experiments to determine the catalyticactivity.

The selected areaelectron diffraction (SAED) and high resolution electron microscopy (HREM) ofthe samples were carried out in a transmission electron microscope (TEM) operating at 300 kV (Jeol, JEM-2200FS).

The temporal analysis of products(TAP) experiments are performed in a quartz micro-reactor, with 33mm bed-lengthand 4.75mm inner diameter, evacuated to 10^{-4} 10^{-5} Pa. Avery small amount of reactant molecules (~10^{-9} mol), which is ~5orders less than the active sites in the catalyst, is pulsed into the reactor bymeans of two high-speed pulse valves. The products and reactants at the outletof the reactor are monitored by a quadrupole mass spectrometer. A temperaturerange of 723K -873K is covered. To study the activity of the $CuO-CeO_2/\gamma-Al_2O_3$,$CuO/\gamma-Al_2O_3$ and $CeO_2/\gamma-Al_2O_3$ catalysts towards toluene totaloxidation, experiments were performed over O_2 pre-treated catalystsby pulsing C_7H_8 with and without di-oxygen in the feed. Typically, a stoichiometric ratioof di-oxygen to toluene, 9:1, was used in the mixture $C_7H_8/O_2/Ar$,when experiments were conducted in the presence of di-oxygen.

In situ XAS experiments wereperformed at the SAMBA beam line of the SOLEIL synchrotron. X-ray absorptionnear edge (XANES) spectra were recorded with 1s time resolution during H_2reduction and reoxidation with CO_2 and water at both the Cu K (8979 eV)and Ce L_{III} edge (5723 eV).

Results

XRD analysis of the$CuO-CeO_2/\gamma-Al_2O_3$ catalyst shows thatalumina and ceria have a crystallite diameter of about 5 nm. At the same time CuO presents singlecrystals of about 100nm. From the STEM and SAD images the CuO single crystalunits of ~100nm were confirmed, while CeO_2appeared as 100nm clusters of nanocrystallites. EDX line scans were undertakenthrough specific regions of a STEM frame, displaying the elements present alongthe line (see Fig.1). The line scan proves that in addition to the large CuO crystallites,°CuO is also present inside the CeO_2 clusters as small sizedspecies. In situ XANES measurements at the CeL_{III} and Cu K edgeyield direct evidence that CeO_2 in the $CuO-CeO_2/g-Al_2O_3$ catalystis reduced by H_2 at similar temperature as the CuO phase. Fig. 2shows XANES results which confirms partial reoxidation of ceria by water. Whereas,CuO is not reoxidised by water.

The toluene oxidation experimentaldata indicate that the reaction is carried out according to a redox Mars-vanKrevelen mechanism. Lattice oxygen atoms from the surface of the catalyst areconsumed by toluene and oxygen vacancies are created. These vacancies arefilled by the oxygen atoms that diffuse from the bulk to the surface of thecatalyst or by di-oxygen. It is shown that the degree of reduction of the metaloxide determines to a large extent its performance for VOCs oxidation. Thepresence of water or CO_2 on the catalyst surface decreases the rateof regeneration of the reduced catalyst by di-oxygen. Furthermore, if waterand/or CO_2 are present in the gas phase, the rate of desorption fromthe surface becomes slower due to the high partial pressure of water in the gasphase.

The activity of the$CuO-CeO_2/Al_2O_3$ catalyst increases in the presenceof H_2O or CO_2. On the other hand, CuO/Al_2O_3showed loss of activity in the presence of H_2O. There was nosignificant changes in activity on CuO/Al_2O_3 and $CeO_2/Al_2O_3$when co-feeding toluene with CO_2.

Conclusions

Two CuO phases existin the CuO-CeO_2/Al_2O_3 catalyst: large ~100nm crystals, not contacting CeO_2 and small CuO speciesdispersed upon and incorporated into clusters of CeO_2nano-crystallites with size ~5nm.

Theeffect of CeO_2 on the catalytic activity can be explained by twofactors. First, ceria stabilizes the dispersion of the active component, i.e. asmaller crystallite size of the CuO phase on the support becomes one of the keyfactors in determining the chemical reactivity. Second, incorporation of copperinto the CeO_2 lattice can form $Ce_{1-x}Cu_xO_{2-d}$solid solution which also has high activity and reducibility at lowertemperatures compared to CuO or CeO_2 alone. The promoting effect ofceria is found to be more pronounced at low temperatures.

AddingH_2O or CO_2 into the C_7H_8/O_2mixture increases the catalytic activity of CuO-CeO_2/Al_2O_3catalyst by producing lattice oxygen species from reoxidation of ceria by CO_2or H_2O. Over the CuO/Al_2O_3catalyst the re-oxidizing role of CO_2 or H_2Oco-fed with toluene is insignificant.

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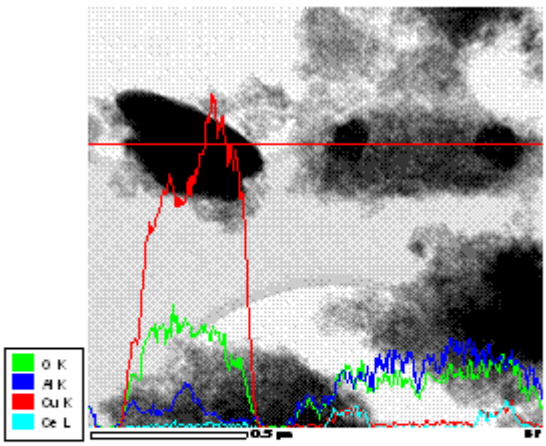

Fig. 1 EDX line scans through a STEM frame on the $CuO-CeO_2/Al_2O_3$ catalyst

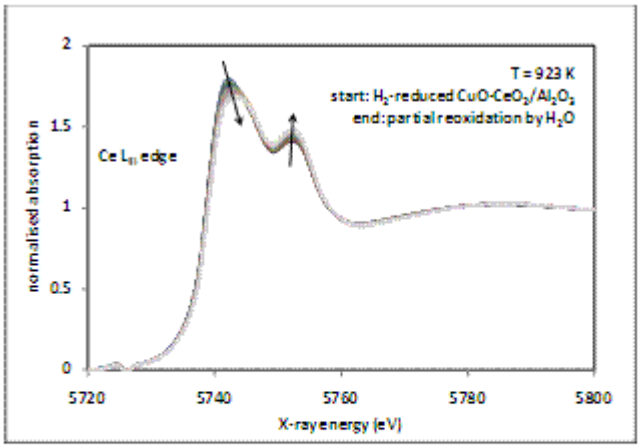

Fig. 2 CO_2 yield and ratio of CO_2 yields vs reaction temperature for experiments with and without H_2O in the feed over $CuO-CeO_2/Al_2O_3$ catalyst

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